Superconductivity and microstructure of epitaxial 
\((\text{Tl,Bi})\text{Sr}_{1.6}\text{Ba}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_{9-\delta}\) thin films

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Abstract

Epitaxial \((\text{Tl,Bi})\text{Sr}_{1.6}\text{Ba}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_{9-\delta}\) ((Tl,Bi)-1223) thin films on (100) single crystal LaAlO\(_3\) substrates were successfully synthesized by a two-step procedure. The (Tl,Bi)-1223 phase development in both air and argon was systematically investigated by X-ray diffraction. The microstructure and epitaxial relationship between films and substrates were measured by X-ray \(\phi\) scan, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The DC resistance versus temperature transition, zero-field-cooled (ZFC) and field-cooled (FC) magnetization transition, hysteresis curve, and transport critical current density were measured. The zero-resistance transition temperature was 107 K, and the critical current density at 77 K and zero field was higher than \(2 \times 10^6\) A/cm\(^2\). (Tl,Bi)-1223 films have good flux-pinning properties as shown by the slow decrease of the critical current density in an external magnetic field.

1. Introduction

Since the TIBaCaCuO superconducting system was discovered [1], several kinds of high-quality thin films of Tl-1212 [2–5], Tl-2212 [6–12], Tl-2223 [13,14] have been reported. Lately, a few groups have paid more attention to Tl-1223 because of its good flux-pinning properties, which are comparable to those of YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) (YBCO), and higher \(T_c\) than YBCO [15–25]. The superior flux-pinning properties are believed to be due to the strong coupling of double Cu–O layers with only a single Tl–O layer between them [26–28]. Consequently, Tl-1223 is a possible candidate for practical applications. Uniform Ag sheathed Tl-1223 superconducting tapes [29] and superconducting thick films [20] have both been successfully fabricated. Although in the absence of an external magnetic field the superconductors exhibit a critical current density \((J_c)\) of \(10^4\) to \(10^5\) A/cm\(^2\) at 77 K, the observed \(J_c\) decreased by a factor of 10 to 20 even in a weak field of 0.2 T at 77 K, due to the presence of weak links in these samples. Recently we have made epitaxial \((\text{Tl,Bi})\text{Sr}_{1.6}\text{Ba}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_{9-\delta}\) ((Tl,Bi)-1223) thin films on (100) single-crystal LaAlO\(_3\) substrates with high critical current density in magnetic field at 77 K and essentially without weak links [30]. In this paper we report:

1. a systematic X-ray diffraction (XRD) and transmission electron microscopy (TEM) study of Tl-1223 phase development in these high-\(J_c\) films as
a function of annealing temperature and annealing duration in air;
(2) the phase development in argon;
(3) the effect of the film thickness on the phase development;
(4) microstructure and superconducting properties of these (Tl,Bi)-1223 films.

2. Experimental

These films of composition (Tl,Bi)Sr_{1.6}Ba_{0.4}Ca_{2-}\text{Cu}_3O_{9-\delta} were prepared by laser ablation in the following way. A superconducting pellet of composition Tl_{0.95}Bi_{0.22}Sr_{1.6}Ba_{0.4}Ca_{2-}\text{Cu}_3O_{9-\delta} was prepared by pressing an intimate mixture of (0.475) Tl_2O_3 + (0.11)Bi_2O_3 + Sr_{1.6}Ba_{0.4}Ca_{2-}\text{Cu}_3O_{7-\delta} in a 1.28 cm diameter die at 1.5 × 10^8 Pa, subsequently placed between gold plates, wrapped in silver foil, and sintered in air at 870–900°C for 3–5 h. The cooled superconducting pellet was pulverized. The source pellet for film fabrication by the laser ablation method was made by mixing 1 FW of the above superconducting powder with 0.475 FW Tl_2O_3 and 0.4 FW CaO, and pressed at 7.5 × 10^8 Pa in a 1.28 cm diameter die. The laser ablation was conducted at 120 mJ/pulse, 21 kV and 2–10 pulses/s at a substrate of temperature 300–500°C. The film was deposited on the (100) surface of single-crystalline LaAlO_3 substrates. The resulting film was placed on a gold plate sitting between two similarly placed unfired pellets of Tl_{0.95}Bi_{0.22}Sr_{1.6}Ba_{0.4}Ca_{2-}\text{Cu}_3O_{9-\delta}. The assembly was wrapped in silver foil with adequate air space for vapor diffusion, and heated in air at 840–870°C for 25–60 min or in argon at 750–780°C for 30 min.

The phase structure and mosaic distribution were measured by X-ray diffraction and rocking curve. The epitaxial relationship between the films and substrates was determined by both X-ray φ scan and transmission electron microscopy (TEM). The microstructural characterization was investigated by both scanning electron microscopy (SEM) and TEM. Both the magnetization versus temperature curve and the hysteresis curve were measured with a DC-SQUID system. The DC zero-resistance temperature T_c and the transport J_c were measured by a standard four-point method. Films were patterned into a 90 μm wide and 200 μm long microbridge by photolithography, and four silver contacts were deposited onto each of the films. The measurements of J_c(H) were made in a magnetic field aligned perpendicular to the c-axis of the films.

3. Results and discussion

3.1. Phase development in air

Fig. 1(a) shows the scanning electron microscopic morphology of the precursor film. The film contained uniformly small particles, a typical morphology of films grown by laser ablation. Although the ablation source was Tl rich with Tl_{1.8}Bi_{0.2}Sr_{1.6}Ba_{0.4}Ca_{2-}\text{Cu}_3O_{9-\delta}, the content of Tl in the precursor films was still lower than 1223 stoichiometry (Table 1). Figs. 1(b) and (c) show the morphology of the annealed films. The uniform round grains were dominant, while a certain amount of a-axis oriented needle-like grains was also observed. Usually the amount of needle-like grains increases as the film becomes thicker. The average composition, determined by EDAX, of the annealed films with few needle-like grains was 0.9 : 1.9 : 2.3 : 2.9, which was close to 1223. The films with more needle-like grains had an average composition of 0.9 : 1.8 : 2.8 : 2.9, which was farther from 1223 stoichiometry.

The annealing temperature is a key parameter for (Tl,Bi)-1223 (1223) phase development. In order to study the effect of annealing temperature, several precursor films were annealed in air for 1 h at different temperatures. At low temperature (820°C), we obtained only pure (Tl,Bi)-1212(1212) phase. As the temperature was increased the 1223 phase gradually formed, which is shown in Fig. 2. At 840°C the sample consisted of both 1223 and 1212 phases. Although the 1223 phase was dominant, the X-ray diffraction (XRD) peaks of 1212 phase was still quite strong, as shown by the intensity of the (004) peak of 1212 phase relative to that of the (005) peak of 1223 phase and that of the (005) peak of 1212 phase relative to that of the (006) peak of 1223 phase. At 850°C the (004) intensity of peak of 1212 phase was only half of that of (005) peak of 1223 phase, and that of (005) peak of 1212 phase was less
Table 1

<table>
<thead>
<tr>
<th></th>
<th>Tl</th>
<th>Bi</th>
<th>Sr</th>
<th>Ba</th>
<th>Ca</th>
<th>Cu</th>
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<tr>
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<td>0.2</td>
<td>1.6</td>
<td>0.3</td>
<td>2.7</td>
<td>2.5</td>
</tr>
<tr>
<td>Annealed film 1</td>
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<td>0.2</td>
<td>1.6</td>
<td>0.4</td>
<td>2.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Annealed film 2</td>
<td>0.7</td>
<td>0.2</td>
<td>1.6</td>
<td>0.2</td>
<td>2.8</td>
<td>2.5</td>
</tr>
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Note: The annealed film 1 has less needle-like grains, while the annealed film 2 has more needle-like grains.

annealing time. At the early stage of annealing the 1212 phase formed first as shown in Fig. 3 (10 min). With longer annealing time, the amount of 1212 phase gradually decreased and more and more 1223 phase formed, which is shown clearly by the relative intensities of peaks (004) and (005) of 1212 phase relative to those of the peaks (005) and (006) of 1223 phase. After 60 min of annealing 1212 phase completely transformed into 1223 phase. We also measured the rocking curves of the (006) reflections of those 1223 films annealed for different lengths of annealing time. At the beginning the FWHM (full width at half maximum) of the rocking curves was large due to poor crystallization of 1223 phase. When the 1223 phase gradually developed the FWHM reached a minimal value of 0.365°, then it

![Fig. 1. SEM morphology of both the precursor and the annealed films.](image)

![Fig. 2. X-ray θ–2θ scans of films annealed at different temperatures. Only (00l) peaks are present; (Tl,Bi)-1223 is marked by filled circles, (Tl,Bi)-1212 by open circles.](image)
slightly increased with longer annealing time due to misorientation.

Based on the results discussed above, we concluded that the optimum annealing temperature and length of annealing time are 860°C and 60 min, respectively.

3.2. Phase development in argon

Post-annealing is the most important step in forming 1223 phase because the precursor films were prepared at low temperature, about 400°C, and in a vacuum chamber lacking in Tl vapor. In order to form the 1223 phase by the post-annealing in air, each precursor film was heated at a high temperature (840–870°C) in a gold boat with two unfired Tl0.95Bi0.22Sr1.8Ba0.4Ca2Cu3O9-δ pellets, and the assembly was wrapped with silver foil. In argon, we annealed the precursor films for the same time duration (30 min) but at different temperatures. However, Fig. 4 shows that the annealing temperature can be dramatically reduced in argon. As reported previously in air the 1212 phase formed first, then 1223 grew at higher temperature [30]. Usually the 1212 phase formed at 820°C in air, but in argon we could
get pure Tl-1212 phase at 730°C as shown in Fig. 4(a). As the temperature was increased the 1223 phase gradually formed. At 740°C the sample consisted of both 1223 and 1212 phases, but Tl-1212 was dominant (Fig. 4(b)). As the temperature was increased to 750°C, the dominant phase became 1223 (Fig. 4(c)). Although the majority of the film material was 1223, the X-ray diffraction (XRD) peaks of the 1212 phase were still quite strong. At 760°C the intensity of the (005) peak for the 1212 phase was only one fourth of that of the (006) peak of the 1223 phase, which means that the 1212 phase was scarce (Fig. 4(d)). As the temperature reached 770°C, the peaks of Tl-1212 were almost invisible, and we got almost pure (Tl, Bi)-1223 films in argon (Fig. 4(e)). At 780°C, very pure (Tl, Bi)-1223 films were obtained in argon (Fig. 4(f)).

The FWHM values of rocking curves of the (006) reflections of 1223 films varied with annealing temperature. At a lower temperature, 760°C, the FWHM was 0.409°, but there still was a little 1212 phase. When pure 1223 phase formed at 770°C, the FWHM was 0.426° which is slightly broader than at the lower temperature.

3.3. Effect of film thickness on phase development

Compared to other high-$T_c$ materials, there is a stronger correlation of 1223 phase development to film thickness. In order to investigate the correlation, the precursor films with different thicknesses were annealed at 860°C for 45 min in air. Fig. 5 shows the dependence of 1223 phase development on film thickness. Films used in Figs. 5(a), (b), (c), and (d) are 0.5, 0.7, 0.95, and 1.2 μm thick, respectively. Apparently when the film was 0.5 μm thick only pure 1212 phase formed. As the film thickness was increased from 0.5 to 0.7 μm, 1223 phase started to form. With further increase of the film thickness to 0.95 μm almost pure 1223 phase was obtained, but very weak peaks of 1212 phase were still detectable. When the film thickness was larger than 1.0 μm, for example, 1.2 μm, 1212 phase completely transformed into 1223 phase as shown in Fig. 5(d). This kind of phenomenon has not been observed in making other high-temperature superconducting films, such as YBCO and BiSrCaCuO. As far as we know the thickness does not affect the phase formation when the composition was kept unchanged in the fabrication of other high-temperature superconductors. For example, no matter how thin the film is,
even under 100 Å, the 123 phase always forms if the composition is $YBa_2Cu_3O_{7-\delta}$. In the present case, the mean composition of the films with different thicknesses is about the same as measured by EDAX (data not shown here). The only recognizable difference is that $T_1$ is less when the film is thinner. But

Fig. 7. TEM photographs of (a) a typical area of epitaxially grown (Tl,Bi)-1223 films and (b) dislocations in films near the film–substrate interface.
this should not make so much difference in phase formation since additional T1 would be incorporated during the annealing step from the unfired pellets sitting alongside the film. Furthermore, almost pure 1223 phase was formed in a two-zone furnace in which the precursor film did not contain T1 at all [20]. More experiments are under way to investigate this new phenomenon.

Fig. 8. High-resolution TEM photographs of (a) semi-periodic lattice strain caused by lattice mismatch between (Tl,Bi)-1223 film and LaAlO₃ substrate, and (b) dislocations near the interface and stacking faults in the upper layer of the film.
3.4. Microstructure and orientation

From the X-ray diffraction patterns, it was obvious that the films were highly phase pure and excellently c-axis oriented. We have also investigated the epitaxial relationship between the films and substrates by both X-ray ϕ scan and transmission electron microscopy (TEM). In order to determine the in-plane orientation between (Tl,Bi)-1223 film and LaAlO₃ substrate we measured the ϕ scans of both the (103) reflection of (Tl,Bi)-1223 and the (222) reflection of LaAlO₃. The results are shown in Figs. 6(a) and (b). From these patterns it was deduced that the [100] axis of (Tl,Bi)-1223 overlapped with [100] of LaAlO₃. This observed epitaxial growth is reasonable, because the lattice mismatch between [100] of (Tl,Bi)-1223 and [100] of LaAlO₃ is only 0.5%.

Fig. 7(a) shows a typical area of the epitaxial film and a misoriented grain. This misoriented grain could be either intrinsic or caused by sample preparation. Fig. 7(b) shows dislocations within the film near the interface. Fig. 8(a) is a high-resolution image of the interface. The contrast is due to strain caused by the lattice mismatch between the film and the single-crystal substrate. Fig. 8(b) shows a thin layer near the interface containing dislocations and a region above the layer containing many stacking faults.

3.5. Superconductivity

Fig. 9 shows a typical DC resistance versus temperature curve measured by a standard four-point method. The zero-resistance transition temperature \( T_c \) was 107 K. Among the many measurements we found that samples with pure (Tl,Bi)-1223 phase have a lower \( T_c \) in the range of 105–107 K, while the films with a little (Tl,Bi)-1212 phase have a higher \( T_c \) about 111 K. This has not been clearly understood yet.

Fig. 10 shows a typical zero-field-cooled (ZFC) and field-cooled (FC) magnetization transition curve measured at 20 G with \( H \) parallel to the c-axis of (Tl,Bi)-1223 film in a DC-SQUID system. The onset transition temperature was 105 K which was lower than the DC zero-resistance \( T_c \) of 107 K. If we assume the flux exclusion was 100% at the lowest measured temperature of the ZFC curve, the flux expulsion measured by FC was nearly 3%, which was seriously incomplete flux expulsion. Incomplete flux expulsion could originate from many reasons such as flux pinning, the Ebner–Stroud superconducting glass model, and not full superconductivity of samples [31]. The last two causes require the presence of weak links. The transport \( J_c \) data discussed below indicate the absence of significant weak links in our films and suggest the observed incomplete flux expulsion could be due to strong flux pinning in the (Tl,Bi)-1223 films.

Fig. 11 shows a half hysteresis curve measured at 4.2 K with \( H \) parallel to the c-axis of the films. The magnetization critical current density \( (J_{cm}) \) of this film, derived from Bean's model, was \( 9 \times 10^6 \) A/cm² at 5.5 T and 4.2 K. This weak field dependence of \( J_{cm} \) at 4.2 K further confirmed that there existed strong flux-pinning centers in the (Tl,Bi)-1223 films.
In high-temperature superconductors many kinds of defects were observed to be effective pinning centers such as twin boundaries \[32\], a-axis oriented plates \[33\] as well as the intrinsic pinning between Cu–O layers \[34\]. In (TI,Bi)-1223 films, fine a-axis oriented plates, dislocations, stacking faults and other defects were observed (shown in Figs. 7 and 8). Their fine scale and high density may partly be responsible for the good pinning properties of (TI,Bi)-1223 films.

The measurements of \( J_c(H) \) are shown in Fig. 12. At three temperatures (67 K, 77 K and 87 K), no obvious \( J_c \) drop was observed in low field (< 0.1 T). At 77 K and 5.5 T, \( J_c \) was \( 5 \times 10^5 \) A/cm\(^2\). Even at 87 K and 5.5 T \( J_c \) was still above \( 10^5 \) A/cm\(^2\). Due to the limitation imposed by the chamber size of the DC-SQUID system, we only managed to measure \( J_c \) with \( H \) perpendicular to the c-axis. A comparison of \( J_c (H \perp c\text{-axis}) \) and \( J_c (H \parallel c\text{-axis}) \) was only obtained at a low magnetic field (0.5 T) using a Varian electromagnet \[30\]. With \( H \) perpendicular to the c-axis \( J_c \) was still almost independent of field, while it dropped rapidly at low field (below 0.1 T) as \( H \) became aligned parallel to the c-axis. Then it decreased slowly above 0.1 T. Comparing with the \( J_c(H) \) behavior of a high-quality YBCO film \[35\], we noted two distinct features. First, there was a big difference between \( J_c(H \perp c\text{-axis}) \) and \( J_c(H \parallel c\text{-axis}) \), which shows that (TI,Bi)-1223 is more anisotropic than YBCO. Second, a surprising \( J_c(H) \) behavior was observed with \( H \) perpendicular to the c-axis. Usually, \( J_c \) drops at a low field and then keeps almost constant after the field reaches a value such as 0.5 T. In (TI,Bi)-1223 films, an obvious drop was not observed. This has not been clearly understood.

4. Conclusion

\((\text{TI,Bi})\text{Sr}_{1.6}\text{Ba}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_{9-\delta}\) films have been successfully grown on (100) \( \text{LaAlO}_3 \) single-crystal substrates by annealing in both air and argon. In addition, we observed the dependence of the phase development on the film thickness. Both c-axis orientation and in-plane alignment have been achieved. The values of \( T_c \) (zero resistance) were in a range of 105–111 K depending on the phase purity. Samples with a little 1212 phase have a higher \( T_c \) of about 111 K, while samples with pure TI-1223 phase have a lower \( T_c \) of 105–107 K. The critical current density \( (J_c) \) at 77 K and zero field reached \( 2 \times 10^6 \) A/cm\(^2\) when measured on a 1 \( \mu \)m thick, 90 \( \mu \)m wide, 200 \( \mu \)m long microbridge. \( J_c \) was still \( 5 \times 10^5 \) A/cm\(^2\) with a 5.5 T magnetic field applied perpendicular to the c-axis.

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References